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Structural, dielectric and magnetic properties of $Ba_3SrLn_2Fe_2Nb_8O_{30}$ (Ln = La, Nd, Sm) filled tungsten bronze ceramics

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ABSTRACT

Structural, dielectric and magnetic properties have been investigated for $Ba_3SrLn_2Fe_2Nb_8O_{30}$ (Ln = La, Nd, Sm) ceramics. The single phase tetragonal filled tungsten bronze structure in space group *P4/mbm* is obtained for $Ba_3SrLa_2Fe_2Nb_8O_{30}$, while such tungsten bronze major phase is determined together with minor amount of secondary phases in $Ba_3SrNd_2Fe_2Nb_8O_{30}$ and $Ba_3SrSm_2Fe_2Nb_8O_{30}$. The saturated magnetic hysteresis loops with enhanced M_r are obtained in the present ceramics at room temperature comparing to the $Ba_4Ln_2Fe_2Nb_8O_{30}$ (Ln = La, Nd, Sm) ceramics. Meanwhile, the typical relaxor behaviors are determined: a broad dielectric peak with strong frequency dispersion and the peak temperature following well with the Vogel–Fulcher relationship.

1. Introduction

Ceramics with tungsten bronze structure compose one of the largest classes of dielectrics just next to the perovskites, and they consist of ten distorted BO_6 octahedra sharing corners. The octahedra are linked by their corners in such a way that three different types of tunnels run right through the structure parallel to the c-axis in a general formula $[(A_1)_2(A_2)_4C_4][(B_1)_2(B_2)_8]O_{30}$ [1]. As the smallest interstice C is generally empty, the filled tungsten bronze structure could have a general formula $A_6B_{10}O_{30}$. These features make them capable of performing a wide range of substitutions, either in the channels or within the octahedral network itself. Thus the properties of tungsten bronzes could be modified further to make it interesting and useful for devices because of the great flexibility of structure.

Recently, Zhu et al. published a comprehensive review on the ferroelectric transition and low-temperature dielectric relaxations in filled tungsten bronze ceramics together with the possible multiferroicity [2]. The ferroelectric nature of $M_4R_2Ti_4Nb_6O_{30}$ and $M_5RTi_3Nb_7O_{30}$ tungsten bronzes have been intensively investigated [3–10]. It is believed that the phase transition nature and transition temperature are primarily determined by structural modulation through the oxygen octahedral tilting [2]. A large radius difference between A1-and A2-site ions (Δr) will lead to the commensurate modulation in tetragonal tungsten bronze structure and the normal ferroelectric transition with a high T_C. The ferroelectric nature changes from normal ferroelectric toward diffuse and relaxor ferroelectric in the tetragonal tungsten bronze structures with incommensurate modulation as Δr decreases. The order of ferroelectric transition in filled tungsten bronzes will also be disturbed by the order/disorder in A1 and A2 sites, their random cross occupancy, and the order/disorder in B-sites.

The filled tungsten bronze ceramics have also been investigated as the possible multiferroic materials by introducing magnetic elements [11–17]. The electrical polarization and ferroelectricity are associated with the off center displacement of the B site cations and octahedra distortion. Meanwhile, the magnetism are associated with magnetic ions with partially filled d shells. Josse et al. reported the coexistence of room-temperature ferromagnetism and ferroelectricity in $Ba_4Ln_2Fe_2Nb_8O_{30}$ (Ln = Nd, Sm, Eu, Gd, and Pr) [12]. In $Ba_4Ln_2Fe_2Nb_8O_{30}$ compounds, the ordered tungsten bronze structure is generally indicated, in which Ba and Ln ions properly occupy the A2 and A1 site, respectively. The problem is that the magnetism is weak for these materials in practical application. The $Ba_4La_2Fe_2Nb_8O_{30}$ compound is paramagnetic with M_{2T} of 0.09 emu/g at room temperature. In $Ba_4Nd_2Fe_2Nb_8O_{30}$ compound, M_r = 0.10 emu/g and H_C = 1860 Oe is obtained with M_{2T} of 0.34 emu/g. M_r = 0.15 emu/g and H_C = 2150 Oe is obtained in $Ba_4Sm_2Fe_2Nb_8O_{30}$

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compound with M_{2T} of 0.42 emu/g [12]. Whether the disturbance of order/disorder in A and B sites have effects on the ferroelectric or magnetic nature are not confirmed in Fe-based filled tungsten bronze ceramics. There is an important issue to further understand how do the cations occupations affect these properties. A convenient way to determine this issue is to substitute one Ba^{2+} cation by smaller Sr^{2+} and then to investigate the variation of properties in $Ba_3SrLn_2Fe_2Nb_8O_{30}$ to form the filled tungsten bronze structures with disordered distribution in A site.

In the present work, dielectric and magnetic characteristics of $Ba_3SrLn_2Fe_2Nb_8O_{30}$ (Ln = La, Nd, Sm) ceramics are investigated together with the structure. The Vogel–Fulcher law and Curie–Weiss law fittings confirm the relaxor nature, and all compositions display the improved magnetic hysteresis loops at room temperature.

2. Material and methods

$Ba_3SrLn_2Fe_2Nb_8O_{30}$ (Ln = La, Nd, Sm) ceramics were prepared by a standard solid–state reaction process. High-purity $BaCO_3$ (99.93%), $SrCO_3$ (99.95%), La_2O_3 (99.99%), Nd_2O_3 (99.99%), Sm_2O_3 (99.99%), Fe_2O_3 (99.9%), and Nb_2O_5 (99.99%) powders were used as the raw materials. Before weighing, La_2O_3, Nd_2O_3 and Sm_2O_3 raw powders were pretreated at 1273 K in air for 3 h to remove the hydroxides. These raw powders were mixed by ball milling in a polyethylene jar with ZrO_2 media in ethanol for 24 h. Then the mixtures were calcined in a high-purity alumina crucible at 1473–1623 K (depending on composition) in air for 3 h. The calcined powders were ground again to reach the homogeneous granulometric distribution. Adding with 6 wt% polyvinyl alcohol (PVA) as the binder, the reground powders were pressed into disks with 12 mm in diameter and 2 mm in thickness under a pressure of about 98 MPa. These discs were sintered at 1523–1623 K in air for 3 h to yield the dense ceramics.

The crystal structure was identified by powder X-ray diffraction (XRD) analysis with Cu Kα radiation (PANalytical, Almelo, the Netherlands) at room temperature. For structure refinement, the XRD data were collected over the range of $2\theta = 10–130°$ with a step width of 0.01°. The Rietveld structural refinement was performed using the FULLPROF program. The microstructures were evaluated by a scanning electron microscopy (S-4800, Hitachi, Tokyo, Japan).

Dielectric characteristics of $Ba_3SrLn_2Fe_2Nb_8O_{30}$ (Ln = Nd and Sm) ceramics were measured with a broadband dielectric spectrometer (Turnkey Concept 50, Novocontrol Technologies, Hundsangen, Germany) in a broad temperature (133–573 K) and frequency (1 Hz–5 MHz) range. The low-temperature dielectric characteristics of $Ba_3SrLa_2Fe_2Nb_8O_{30}$ ceramics were measured with an impedance analyzer (Agilent4294A, Agilent Technologies Inc., Santa Clara, CA) equipped with a cooling system (HC-4E 1, Janis, Woburn, Massachusetts) in a temperature (30–200 K) and frequency (100 kHz–1 MHz) range. The magnetization measurements were conducted with a magnetic property measurement system (MPMS-XL-5, Quantum Design, San Diego, CA) in a temperature (10–300 K) range.

3. Results and discussion

3.1. Phase and structure analysis

Fig. 1 shows the XRD patterns of the polycrystalline $Ba_3SrLn_2Fe_2Nb_8O_{30}$ (Ln = La, Nd, Sm) ceramics. The tetragonal tungsten bronze single phase structure is determined for Ln = La, while a few additional peaks of $LnNbO_4$ are observed for the compositions of Ln = Nd and Sm beside the tungsten bronze major phase. The phase fraction of $LnNbO_4$ is approximately 2% for Ln = Nd and 7% for

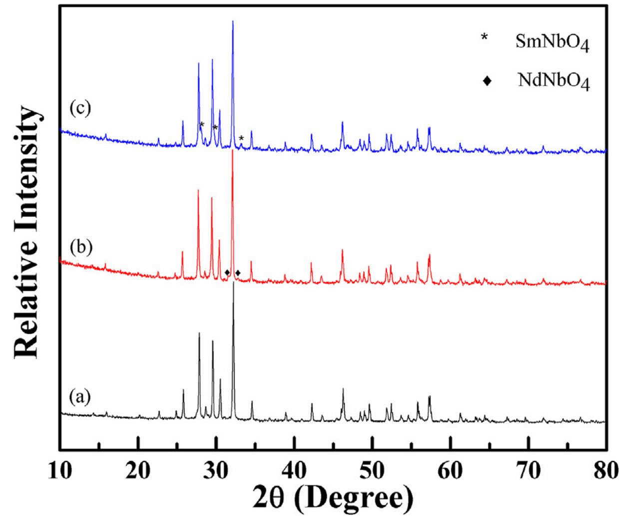

Fig. 1. XRD patterns of crashed powders of $Ba_3SrLn_2Fe_2Nb_8O_{30}$ ceramics: a)Ln = La, b) Ln = Nd, and c) Ln = Sm.

Ln = Sm according to a rough estimate. As the ionic radius of rare earth decreases from 0.136 nm (Ln = La) to 0.124 nm (Ln = Sm), the tolerance factors of filled tungsten bronze are diminished from 0.967 to 0.954, while the tolerance factors for A1 site cation are diminished from 0.954 to 0.913, and this results in the reduced structure stability.

The Rietveld refinement of XRD data for $Ba_3SrLa_2Fe_2Nb_8O_{30}$ confirms the tetragonal tungsten bronze structure in space group *P4/mbm* (see Fig. 2). As shown in Table 1, the experimental parameters (R_{wp} = 3.71%, R_p = 2.85%, R_{exp} = 3.02% and χ^2 = 1.51) indicate the fine agreement between the calculated and the observed XRD patterns. The lattice parameters of $Ba_3SrLa_2Fe_2Nb_8O_{30}$ are calculated as $a = b$ = 12.4918(2) Å, c = 3.9309(1) Å, V = 613.395(20) $Å^3$. The selected bond lengths and angles are summarized in Table 2. Since three A2-sites are occupied by Ba ions, the rest of A-sites might be occupied disorderly by Sr and La ions considering the small difference of ion radius between them, which results in a disordered cation distribution. In tetragonal tungsten bronze ferroelectrics, the cation distribution has significant influence on the ferroelectric transition, and the relaxor behavior is closely associated with the disordering in cationic

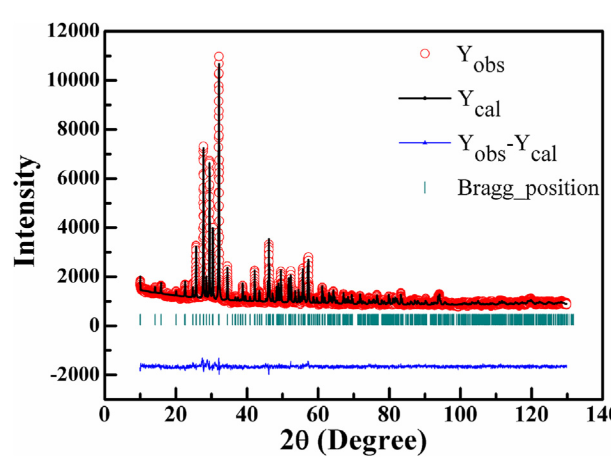

Fig. 2. Observed (open circles), calculated (solid lines), and difference (bottom line) of X-ray powder diffraction patterns for $Ba_3SrLa_2Fe_2Nb_8O_{30}$ ceramics. The tick marks present the position of all possible Bragg reflections of $Ba_3SrLa_2Fe_2Nb_8O_{30}$.